Coupling of Critical Fluctuations with Self-Entanglements in Polymer Solutions

A.F. Kostko[C,S]
Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.

M.A. Anisimov
Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.

J.V. Sengers
Institute for Physical Science and Technology and Department of Chemical Engineering, University of Maryland, College Park, MD, U.S.A.

Accurate and systematic dynamic light-scattering studies of near-critical polystyrene-cyclohexane solutions with the molecular weight of the polymer ranging from 200,000 to 11.4 million have been performed. An avoided crossing of two effective dynamic modes has been observed. These effective modes are generated by a coupling of two soft modes, namely diffusive decay of critical fluctuations and relaxation of self-entanglement of long polymer chains. As a result of the coupling, neither of the effective modes is the original diffusive mode or the self-entanglement mode. This phenomenon is observed when the size of the polymer molecules becomes of the order of the inverse wave number of the critical fluctuations or exceeds it. Characteristic times of the two originally uncoupled modes have been calculated on the basis of Brochard / De Gennes' reptation model for polymer solutions and conventional critical-dynamics theory. We obtain good agreement between theory and experiment after incorporating a crossover from Ising-like critical behavior to tricritical (theta-point) mean-field behavior for both dynamic and static properties. Molecular-weight scaling of the characteristic time of self-entanglements, of the characteristic viscoelastic length, and of the mesoscopic viscosity (that controls the decay rate of critical fluctuations) has been obtained along the line of critical points of the polymer solutions with different degrees of polymerization.

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